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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : DAINIPPON PRINTING CO LTD

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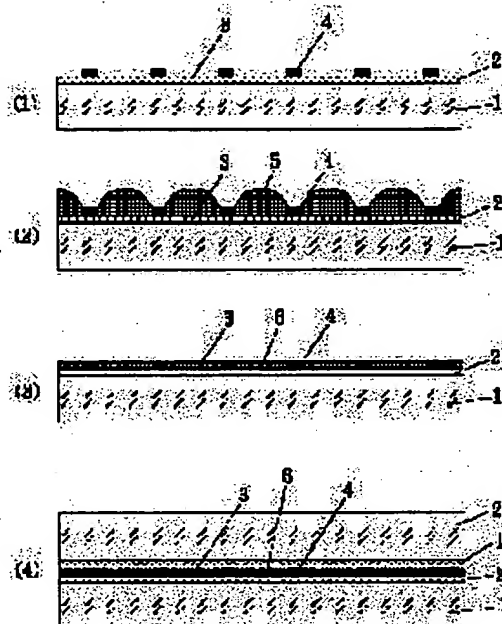
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ANDO MASAYUKI

## (54) LIQUID CRYSTAL OPTICAL ELEMENT AND ITS PRODUCTION

## (57)Abstract:

**PURPOSE:** To provide a liquid crystal optical element which facilitates pattern coating, is small in useless consumption of a liquid crystal emulsion and has an excellent display characteristics by forming a liquid crystal/high polymer composite film only in the hydrophilic part of a conductive substrate.

**CONSTITUTION:** A transparent conductive film 2 is formed on the surface of a transparent substrate 1 and the hydrophilic parts 3 and water repellent parts 4 are formed on the transparent conductive film 2. The transparent conductive film may be used as it is as the hydrophilic parts 3 and the hydrophobicity thereof may be further improved by roughening the surface of the film or forming a hydrophilic film. The liquid crystal emulsion 5 remains only on the hydrophilic parts 3 and does not exist in the water repellent parts 4 if the entire surface of the substrate is coated with the liquid crystal emulsion 5 from which air bubbles are sufficiently removed. The liquid crystal/ high polymer composite films 6 matching the patterns of the hydrophilic parts 3 are obtd. if the coating is dried at room temp. after the application of the liquid crystal emulsion 5. Finally, the transparent conductive film surface of a counter substrate 2' on which the transparent conductive film 1' is formed, is stuck facing the liquid crystal/high polymer combined films 6 to obtain the liquid crystal display element.



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**CLAIMS**

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**[Claim(s)]**

[Claim 1] A liquid crystal optical element which liquid crystal / macromolecule bipolar membrane is the conductive substrates which prepared a hydrophilic portion to which one substrate can apply a liquid crystal emulsion, and a water-repellent portion which flips a liquid crystal emulsion in a liquid crystal optical element which it comes to \*\*\*\* with a conductive substrate of a pair at least with transparent one side, and is characterized by forming liquid crystal / macromolecule bipolar membrane only in a hydrophilic portion of a conductive substrate.

[Claim 2] A manufacture method of a liquid crystal optical element characterized by sticking a counterelectrode after it forms a hydrophilic portion and a water-repellent portion in a transparent electrode side of one substrate of a conductive substrate of a pair, and at least one side applies and dries a liquid crystal emulsion all over these portions being included and forms liquid crystal / macromolecule bipolar membrane only in a hydrophilic portion.

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**DETAILED DESCRIPTION****[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention relates to the liquid crystal optical element which used the liquid crystal / macromolecule bipolar membrane which distributed liquid crystal in the high polymer in more detail about a liquid crystal optical element.

**[0002]**

**[Description of the Prior Art]** Conventionally, since the liquid crystal display has the features, such as a low power, a light weight, and a thin shape, it is broadly used for a wrist watch, a calculator, a personal computer, television, etc. as an alphabetic character or display data medium of an image. Common TN and a common STN mold liquid crystal display enclose liquid crystal into the liquid crystal cell by which the predetermined seal etc. was given between the glass plates of the pair which has a transparent electrode, and are further sandwiched with a polarizing plate from both sides.

**[0003]** However, the above-mentioned conventional liquid crystal display (1) Since an angle of visibility is narrow since two polarizing plates are required, and brightness is insufficient, With large (2) cel thickness dependency which needs the back light of high power consumption, and difficult large-area-izing (3) Since the manufacturing process is complicated, formation of an orientation film, its rubbing processing, enclosure of the liquid crystal to a cel, etc. have problems, like a manufacturing cost is high, and a limit is in lightweight-izing of a liquid crystal display, thin-shape-izing, large-area-izing, low-power-izing, and low cost-ization.

**[0004]** As liquid crystal display data medium which solves such a trouble, application of the liquid crystal / macromolecule bipolar membrane which distributed liquid crystal in the macromolecule matrix was expected, and the research and development have activated. The manufacture method of liquid crystal / macromolecule bipolar membrane can mainly be classified into the emulsion method and a phase separation method. The method (\*\*\*\*\* No. 501631 [ 58 to ] official report) of producing from the aqueous solution which emulsified liquid crystal by using polyvinyl alcohol (PVA) as protective colloid as an emulsion method, the method (JP,60-252687,A) of mixing a liquid crystal emulsion with a latex and producing from an aqueous solution, etc. are mentioned.

**[0005]**

**[Problem(s) to be Solved by the Invention]** Although a bright liquid crystal display element with high efficiency for light utilization is obtained by the method of application, there is a possibility of low-pricing and it can consider by using the emulsion method to the appearance which is an apparently very advantageous method, various problems exist in actual manufacture. Especially, since the spreading fitness of the liquid crystal emulsion itself which is spreading liquid is not desirable, there is a problem that uniform liquid crystal / macromolecule bipolar membrane which was excellent in the property depending on the method of application are not obtained.

**[0006]** the liquid crystal emulsion obtained by mixing and agitating the aqueous solution and liquid crystal of water soluble polymer material -- low [ of driver voltage ] -- although it is carried out by making a liquid crystal component into 80 - 90 % of the weight, and lessening a high polymer component as much as possible in order to raise a lower electro-optics property, removing [ of the air bubbles of the mixed air ] becomes difficult [ a liquid crystal emulsion ], since it has thixotropicality peculiar to the aqueous solution of water soluble polymer material. With a product like a display, existence of air bubbles is a fatal problem, and the air bubbles mixed especially at the time of spreading cannot be removed, but are very difficult to produce commercially. Therefore, it is also difficult to satisfy complete equalization of the voltage characteristic demanded in a liquid crystal optical element.

**[0007]** Moreover, in order to have to lessen the macromolecule matrix component in a liquid crystal emulsion as much as possible, the wettability to the substrate of a liquid crystal emulsion is bad, crawling of liquid arises and formation of

a uniform film is difficult. Thus, since spreading fitness is bad, it is in the condition which various kinds of methods of application cannot apply effectively. For example, in a blade coating method, it begins to apply, and applies, there are troubles, such as the last spreading nonuniformity, and there are a paint film edge and a trouble of using an expensive excessive liquid crystal emulsion still more nearly impossible [ a pattern coat ]. Moreover, in screen printing, there is a trouble of the circumference of the reverse side of the emulsion to generating of the air bubbles in the time of passing a mesh or the rear face of a version. Therefore, the purpose of this invention is offering the liquid crystal optical element excellent in the display property which the trouble of the above-mentioned conventional technology is solved, a pattern coat's is very easy, and there is no waste of a liquid crystal emulsion, and air bubbles' do not contain at all in the liquid crystal / macromolecule bipolar membrane in a liquid crystal optical element.

[0008]

[Means for Solving the Problem] The above-mentioned purpose is attained by the following this inventions. That is, liquid crystal / macromolecule bipolar membrane is the conductive substrates which prepared a hydrophilic portion to which one substrate can apply a liquid crystal emulsion, and a water-repellent portion which flips a liquid crystal emulsion in a liquid crystal optical element which it comes to \*\*\*\* with a conductive substrate of a pair at least with transparent one side, and this inventions are a liquid crystal optical element characterized by forming liquid crystal / macromolecule bipolar membrane only in a hydrophilic portion of a conductive substrate, and its manufacture method.

[0009]

[Function] The hydrophilic portion and the water-repellent portion are formed in the field of the conductive substrate which forms liquid crystal / macromolecule bipolar membrane, and if a liquid crystal emulsion is applied all over these portions being included, a liquid crystal emulsion will be applied only to the above-mentioned hydrophilic portion, and will not be applied to a water-repellent portion. Therefore, an expensive liquid crystal emulsion is not wasted. Moreover, on the occasion of this spreading, since the spreading side is smooth on parenchyma, a liquid crystal emulsion is agitated and air bubbles are not won. And by drying in this condition, liquid crystal / macromolecule bipolar membrane is formed as the pattern of arbitration very easily, and the liquid crystal optical element excellent in the display property can be offered by sticking a counterelectrode on the whole surface after that.

[0010]

[Best Mode of Carrying Out the Invention] Next, a desirable embodiment is mentioned and this invention is explained in more detail. The liquid crystal as used in the field of this invention is organic mixture in which a liquid crystal condition is shown near ordinary temperature, and a nematic liquid crystal, cholesteric liquid crystal, and a smectic liquid crystal are contained. Among these, the nematic liquid crystal which added a nematic liquid crystal or cholesteric liquid crystal is desirable on a property. Such liquid crystal may be microencapsulated. Dichroism coloring matter can also color the above-mentioned liquid crystal. The purpose of the color display by coloring is one of reasons for coloring liquid crystal, and there is also the purpose of raising the contrast of a display image using the difference of the absorption of light at the time of voltage impression and no impressing.

[0011] The thing of the guest host type currently generally used with TN and a STN mold liquid crystal display may be used for the dichroism coloring matter used for coloring, and the coloring matter liquid crystal / for macromolecule bipolar membrane may be used for it. However, the solubility to liquid crystal is large and the solubility to a macromolecule is small, and moreover, although 2 color ratio is large and what has the few absorption at the time of voltage impression is good, since it changes with liquid crystal to be used, it is necessary to determine these properties for every liquid crystal. If there are too many additions of coloring matter, dissolution to a macromolecule will increase, and the color remainder at the time of voltage impression generates and is not desirable. Moreover, if there are too few amounts of coloring matter, the difference of the absorption of light at the time of voltage impression and no impressing becomes small, and the improvement effect of contrast is not enough. Therefore, it is desirable to use it in 0.1 - 5% of the weight of the range to the liquid crystal to be used. Furthermore, it is desirable to make it dissolve in 1 - 3% of the weight of concentration.

[0012] Although the thing conventionally depended on the well-known liquid crystal emulsion method may not be depended on a phase separation method, either and limited especially, as for the liquid crystal emulsion used by this invention, what is depended on the emulsion method is desirable. A liquid crystal emulsion is obtained by carrying out emulsification distribution of said liquid crystal into the aqueous solution containing suitable matrix resin. As a method of making a MATORIKUSU aqueous solution distributing the above-mentioned liquid crystal, the mixed method by various kinds of churning equipments, such as an ultrasonic disperser, and the distributed methods, such as the film emulsifying method (refer to Masataka Tadao Nakajima and Shimizu, PHARMTECH JAPAN 4 volume, and No. 10 (1988)), are effective. Although it is dependent on the distributed method to be used, as for the magnitude of a liquid crystal emulsion particle, it is desirable that it is in the range whose mean particle diameter is generally 0.5-7

micrometers, and it is still more desirable that it is the range which is 1-5 micrometers. As matrix resin used for production of a liquid crystal emulsion, although PVA is used preferably, gelatin, an acrylic-acid copolymer, water-soluble alkyd resin, etc. should just distribute or dissolve in water.

[0013] If the mixing ratios (weight ratio) of matrix resin/liquid crystal are 5 / 95 - 50/50 and there is too little amount of the liquid crystal used as amount of liquid crystal and the matrix resin used In order to change a film into a transparency condition for the transparency at the time of voltage ON not only to to run short, but, it is inadequate in respect of needing great voltage etc., and if there is too much amount of the liquid crystal used, since dispersion at the time of voltage OFF (turbidity) not only runs short, but membranous reinforcement will fall on the other hand, it is not desirable. As a substrate for forming the liquid crystal / macromolecule compound-die optical element of this invention, either is ITO and SnO<sub>2</sub> at least. It is the substrate of pairs, such as glass and a high polymer film, which gave transparency conductivity like a system and a ZnO system.

[0014] Next, the manufacture method of the liquid crystal optical element of this invention is explained. Drawing 1 is desirable drawing of this invention which explains the manufacturing process of a liquid crystal optical element [ like ] in illustration 1 operative condition. First, as shown in drawing 1 (1), the transparency electric conduction films 2, such as an ITO film, are formed in the surface of the transparency substrate 1, and the hydrophilic portion 3 and the water-repellent portion 4 are formed on the transparency electric conduction film 2. ITO and SnO<sub>2</sub> since a transparency conductivity coat like a system and a ZnO system is usually hydrophilicity, you may use it as a hydrophilic portion 3 as it is -- it carries out (example of illustration), and a film surface is split-face-ized, or a hydrophilic coat may be formed and hydrophilicity may be raised further. For example, one example of the desirable formation method of the hydrophilic portion 3 is the method of vapor-depositing metals, such as aluminum, as an about 10-1,000Å very thin film. Such an aluminum film has sufficient hydrophilicity. This vacuum-plating-of-aluminium layer may be formed all over a substrate, and may be formed in the shape of [ of arbitration ] a pattern.

[0015] On the other hand, the water-repellent portion 4 can be made to act as a black matrix after element formation by coloring black necessarily transparently. This water-repellent portion 4 can prepare the ink which consists of \*\*\*\* water repellence materials, such as silicone resin, fluororesin, drying oil, and various resists, and can form it printing and by making it dry and harden with the silk screen etc. in this ink in the shape of [ of arbitration with a thickness of about 0.1-1 micrometer ] a pattern. When it can form in the shape of [ of arbitration ] a pattern on it when said hydrophilic portion 3 is formed in the whole surface, and said hydrophilic portion 3 is formed in the shape of a pattern, this water-repellent portion 4 can be aligned with the rim of this pattern, and printing formation can be carried out. These water-repellent portions 4 have [ like ] the desirable thing which mixing of the color of liquid crystal / macromolecule bipolar membrane and a color formed on the hydrophilic portion 3 which a color differs and adjoins does not produce and which is colored light impermeability nature, although it is not necessary to color even if it colors. Coloring of the water-repellent portion 4 may go in a color, coatings, etc. after production of the water-repellent portion 4, a color may be beforehand dissolved into hydrophobic ink, or it may distribute a pigment etc., and may produce the water-repellent portion 4.

[0016] Next, if the liquid crystal emulsion 5 which fully removed air bubbles is applied all over a substrate, as shown in drawing 1 (2), the liquid crystal emulsion 5 does not exist in the remainder and the water-repellent portion 4 only on the hydrophilic portion 3. As a method of carrying out the liquid crystal emulsion 5 with \*\*, which method may be used for flow casting, brush coating, a spray, blade coating, doctor coating, etc. After applying the liquid crystal emulsion 5, if it is made to dry at the temperature of the degree which does not affect a room temperature or a liquid crystal emulsion, as shown in drawing 1 (3), the liquid crystal / macromolecule bipolar membrane 6 which aligned with the pattern of the hydrophilic portion 3 will be obtained. As for the thickness of such liquid crystal / macromolecule bipolar membrane 6, it is desirable that it is usually about 3-15 micrometers. It is made to stick, without leaving air bubbles and space by turning to above-mentioned liquid crystal / macromolecule bipolar membrane 6 the transparency electric conduction film surface of opposite substrate 2' in which transparency electric conduction film 1' was formed, and sticking it, as shown in the last drawing 1 (4), and the liquid crystal display element of this invention is obtained.

[0017] [Example] Next, an example is given and this invention is explained still more concretely.

the ITO film top of example 1 glass substrate -- the solution of amorphous fluororesin (SAITOPPU CTX-805, product made from Asahi Glass) -- a spin coat method -- the whole surface -- spreading -- and stoving was carried out and the water-repellent portion (thickness: 0.2 micrometers) was formed. Subsequently, it masked except the part which should form the liquid crystal / macromolecule bipolar membrane used as a display, aluminum was vapor-deposited to a part for an outcrop, and the hydrophilic portion (thickness of 100Å) was produced. the whole substrate surface which, on the other hand, produces the liquid crystal emulsion which made the 10-% of the weight aqueous solution of polyvinyl

alcohol KP-06 (Nippon Synthetic Chemical Industry Co., Ltd. make) distribute a nematic liquid crystal (BL-010, Merck Co. make) by the film emulsifying method, and has a water-repellent portion and a hydrophilic portion for this liquid crystal emulsion -- applying - when it was made to dry, liquid crystal / macromolecule bipolar membrane was formed only in the hydrophilic portion by which aluminum was vapor-deposited. Subsequently, the liquid crystal optical element of this invention was produced by laminating a polyethylene terephthalate film with ITO (125 micrometers of thickness, Teijin, Ltd. make) all over liquid crystal / macromolecule bipolar membrane being included, and fixing the perimeter by the ultraviolet curing mold sealing compound. In this liquid crystal optical element, if liquid crystal/poly membrane, and the polyethylene terephthalate film with ITO were stuck completely and this element did not impress voltage, it was white opacity, but when voltage was impressed, it became transparent and colorless promptly.

[0018] it masks except the part which should form the liquid crystal / macromolecule bipolar membrane on a glass substrate with example 2ITO, and amorphous -- in fluororesin SAITOPPU CTX-805 (product made from Asahi Glass), with the dip coating method, coating and after carrying out stoving, masking material was exfoliated, and the hydrophilic portion used as a water-repellent portion (thickness: 0.2 micrometers) and a display was formed. The liquid crystal emulsion which, on the other hand, made the 10-% of the weight aqueous solution of polyvinyl alcohol KP-06 (Nippon Synthetic Chemical Industry Co., Ltd. make) distribute the nematic liquid crystal (BL-010, Merck Co. make) in which dichroism coloring matter (G-264, made in Japanese Sensitizing dye Research institute) was dissolved by the film emulsifying method is produced. This liquid crystal emulsion was applied all over the substrate which has a water-repellent portion and a hydrophilic portion, and when it was made to dry, liquid crystal / macromolecule bipolar membrane was formed only in the ITO portion which is a hydrophilic portion. Subsequently, the liquid crystal optical element of this invention was produced by laminating a polyethylene terephthalate film with ITO (125 micrometers of thickness, Teijin, Ltd. make) all over liquid crystal / macromolecule bipolar membrane being included, and fixing the perimeter by the ultraviolet curing mold sealing compound. In this liquid crystal optical element, if liquid crystal/poly membrane, and the polyethylene terephthalate film with ITO were stuck completely and this element did not impress voltage, it was blue opacity, but when voltage was impressed, it became transparent and colorless promptly.

[0019]

[Effect] According to this invention like \*\*\*\*, the liquid crystal optical element excellent in the display property which a pattern coat is very easy, and there is no waste of a liquid crystal emulsion, and air bubbles do not contain at all in the liquid crystal / macromolecule bipolar membrane in a liquid crystal optical element can be offered.

[0020]

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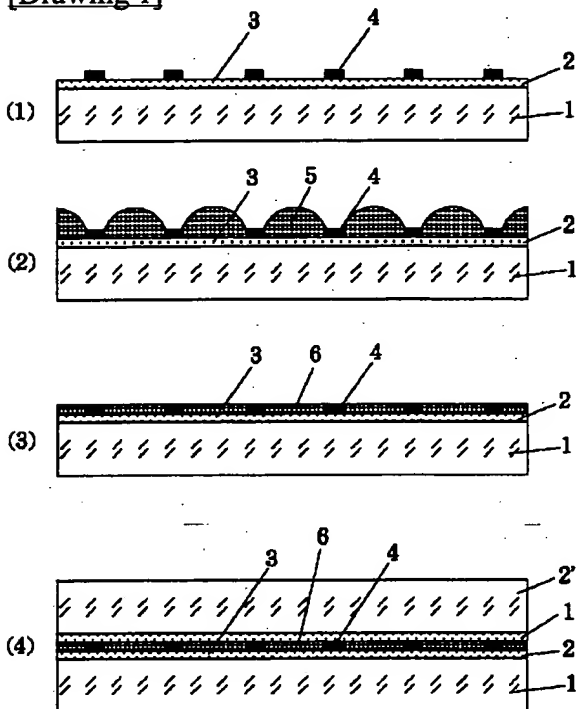
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## DRAWINGS

[Drawing 1]



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## Patent Abstracts of Japan

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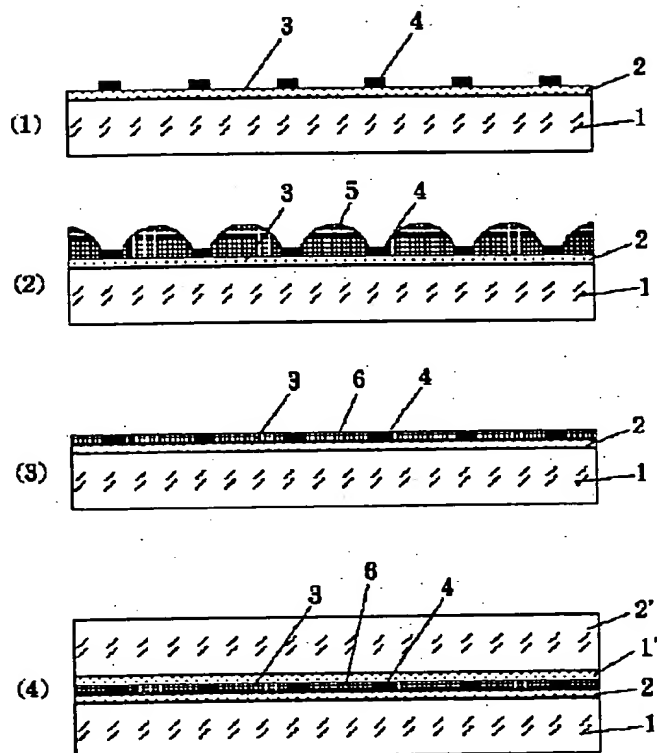
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APPLICANT : DAINIPPON PRINTING CO LTD;

INVENTOR : ANDO MASAYUKI;

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TITLE : LIQUID CRYSTAL OPTICAL ELEMENT  
AND ITS PRODUCTION



ABSTRACT : PURPOSE: To provide a liquid crystal optical element which facilitates pattern coating, is small in useless consumption of a liquid crystal emulsion and has an excellent display characteristics by forming a liquid crystal/high polymer composite film only in the hydrophilic part of a conductive substrate.

CONSTITUTION: A transparent conductive film 2 is formed on the surface of a transparent substrate 1 and the hydrophilic parts 3 and water repellent parts 4 are formed on the transparent conductive film 2. The transparent conductive film may be used as it is as the hydrophilic parts 3 and the hydrophilicity thereof may be further improved by roughening the surface of the film or forming a hydrophilic film. The liquid crystal emulsion 5 remains only on the hydrophilic parts 3 and does not exist in the water repellent parts 4 if the entire surface of the substrate is coated with the liquid crystal emulsion 5 from which air bubbles are sufficiently removed. The liquid crystal/ high polymer composite films 6 matching the patterns of the hydrophilic parts 3 are obtd. if the coating is dried at room temp. after the application of the liquid crystal emulsion 5. Finally, the transparent conductive film surface of a counter substrate 2' on which the transparent conductive film 1' is formed, is stuck facing the liquid crystal/high polymer combined films 6 to obtain the liquid crystal display element.

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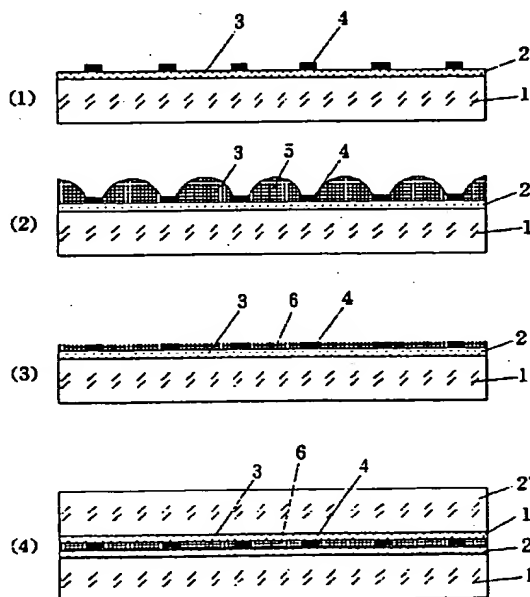
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(54)【発明の名称】 液晶光学素子及びその製造方法

(57)【要約】

【目的】 従来技術の問題点を解決し、パターンコートが極めて容易であり、液晶エマルジョンの浪費がなく且つ液晶光学素子における液晶／高分子複合膜中に気泡が全く含有していない表示特性に優れた液晶光学素子を提供すること。

【構成】 液晶／高分子複合膜が、少なくとも一方が透明である一対の導電性基板で挟持されてなる液晶光学素子において、一方の基板が、液晶エマルジョンを塗布可能な親水性部分と、液晶エマルジョンを弾く撥水性部分とを設けた導電性基板であり、液晶／高分子複合膜が導電性基板の親水性部分にのみ形成されていることを特徴とする液晶光学素子、及びその製造方法。



## 【特許請求の範囲】

【請求項1】 液晶／高分子複合膜が、少なくとも一方が透明である一対の導電性基板で挟持されてなる液晶光学素子において、一方の基板が、液晶エマルジョンを塗布可能な親水性部分と、液晶エマルジョンを弾く撥水性部分とを設けた導電性基板であり、液晶／高分子複合膜が導電性基板の親水性部分にのみ形成されていることを特徴とする液晶光学素子。

【請求項2】 少なくとも一方が透明である一対の導電性基板の一方の基板の電極面に、親水性部分と撥水性部分を形成し、これらの部分を含む全面に液晶エマルジョンを塗布及び乾燥して親水性部分にのみ液晶／高分子複合膜を形成した後対向電極を貼り合わせることを特徴とする液晶光学素子の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は、液晶光学素子に関し、更に詳しくは高分子物質中に液晶を分散させた液晶／高分子複合膜を使用した液晶光学素子に関する。

## 【0002】

【従来の技術】 従来、液晶ディスプレイは、低消費電力、軽量、薄型等の特徴を有している為、文字や画像の表示媒体として、腕時計、電卓、パソコン、テレビ等に幅広く用いられている。一般的なTN及びSTN型液晶ディスプレイは、透明電極を有する一対のガラス板間に所定のシール等が施された液晶セル中に液晶を封入し、更に両面から偏光板でサンドイッチされたものである。

【0003】 しかしながら、上記従来の液晶ディスプレイは、(1)二枚の偏光板が必要な為視野角が狭く、又、輝度が不足している為、高消費電力のバックライトが必要である、(2)セル厚依存性が大きく大面積化が困難である、(3)配向膜の形成、そのラビング処理及びセルへの液晶の封入等、その製造工程が複雑な為に製造コストが高い等の問題があり、液晶ディスプレイの軽量化、薄型化、大面積化、低消費電力化、低コスト化に限界がある。

【0004】 この様な問題点を解決する液晶表示媒体として、液晶を高分子マトリックス中に分散させた液晶／高分子複合膜の応用が期待され、その研究開発が活発化してきた。液晶／高分子複合膜の製造方法は主としてエマルジョン法と相分離法に分類することが出来る。エマルジョン法としては、ポリビニルアルコール(PVA)を保護コロイドとして液晶を乳化した水溶液から作製する方法(特表昭58-501631号公報)、液晶エマルジョンをラテックスと混合して水溶液から作製する方法(特開昭60-252687号公報)等が挙げられる。

## 【0005】

【発明が解決しようとしている問題点】 エマルジョン法を用いることにより、塗布方法によって光利用効率の高

い明るい液晶表示素子が得られ、低価格化の可能性もあって一見極めて有利な方法である様に思えるが、実際の製造においては種々の問題が存在する。特に、塗布液である液晶エマルジョン自体の塗布適性が好ましくない為に、塗布方法によっては特性の優れた均一な液晶／高分子複合膜が得られないという問題がある。

【0006】 水溶性高分子物質の水溶液と液晶とを混合・攪拌して得られる液晶エマルジョンは、駆動電圧の低下等の電気光学特性を向上させる為に、液晶成分を80～90重量%とし高分子物質成分を出来る限り少なくすることで行なわれているが、液晶エマルジョンは水溶性高分子物質の水溶液に特有のチキソトロピック性を有する為に、混入した空気の気泡の除去が困難となる。表示装置の様な製品では気泡の存在は致命的な問題であり、特に塗布時に混入した気泡は除去することが出来ず、製品化が極めて困難である。従って、液晶光学素子において要求される電圧特性の全面均一化を満足させることも困難である。

【0007】 又、液晶エマルジョン中の高分子マトリックス成分を可能な限り少なくしなければならない為に、液晶エマルジョンの基板に対する濡れ性が悪く、液のはじきが生じたりして均一な膜の形成が困難である。この様に塗布適性が悪い為に各種の塗布方法が有効に適用出来ない状況である。例えば、ブレードコーティング法では、塗膜エッジ、塗り始め及び塗り終りの塗布ムラ等の問題点があり、更にパターンコートが不可能で、且つ高価な余分な液晶エマルジョンを使用するという問題点がある。又、スクリーン印刷法ではメッシュを通過する時点で気泡の発生や版の裏面へのエマルジョンの裏回りという問題点がある。従って本発明の目的は、上記従来技術の問題点を解決し、パターンコートが極めて容易であり、液晶エマルジョンの浪費がなく且つ液晶光学素子における液晶／高分子複合膜中に気泡が全く含有していない表示特性に優れた液晶光学素子を提供することである。

## 【0008】

【問題点を解決するための手段】 上記目的は以下の本発明によって達成される。即ち、本発明は、液晶／高分子複合膜が、少なくとも一方が透明である一対の導電性基板で挟持されてなる液晶光学素子において、一方の基板が、液晶エマルジョンを塗布可能な親水性部分と、液晶エマルジョンを弾く撥水性部分とを設けた導電性基板であり、液晶／高分子複合膜が導電性基板の親水性部分にのみ形成されていることを特徴とする液晶光学素子、及びその製造方法である。

## 【0009】

【作用】 液晶／高分子複合膜を形成する導電性基板の面に、親水性部分と撥水性部分を形成しておき、これらの部分を含む全面に液晶エマルジョンを塗布すると、液晶エマルジョンは上記親水性部分のみに塗布され、撥水性

部分には塗布されない。従って高価な液晶エマルジョンを浪費することがない。又、この塗布に際しては塗布面が実質上平滑であるので液晶エマルジョンが攪拌されて気泡を抱き込むことがない。そしてこの状態で乾燥することによって、任意のパターン通りに極めて容易に液晶／高分子複合膜が形成され、その後全面に対向電極を貼り合わせることで、表示特性に優れた液晶光学素子を提供することが出来る。

#### 【0010】

【好ましい実施態様】次に好ましい実施態様を挙げて本発明を更に詳しく説明する。本発明で云う液晶とは、常温付近で液晶状態を示す有機混合物であって、ネマチック液晶、コレステリック液晶、スメクチック液晶が含まれる。このうちネマチック液晶若しくはコレステリック液晶を添加したネマチック液晶が特性上好ましい。これらの液晶はマイクロカプセル化されたものであってもよい。上記の液晶は二色性色素で着色しておくことも出来る。液晶を着色する理由としては、着色によるカラー表示という目的もあるが、電圧印加時と無印加時の光の吸収の差を利用して表示画像のコントラストを高めるという目的もある。

【0011】着色に使用する二色性色素は、TN及びS-TN型液晶ディスプレイで一般的に使用されているゲスト・ホストタイプのものを用いてもよいし、液晶／高分子複合膜用の色素を用いてもよい。但し、液晶への溶解度が大きくて高分子への溶解度が小さく、しかも2色比が大きく、電圧印加時の吸収が少ないものが良いが、これらの特性は、用いる液晶によって異なるので液晶毎に決定する必要がある。色素の添加量が多過ぎると高分子への溶解が多くなり、電圧印加時の色残りが生じて好ましくない。又、色素の量が少な過ぎると電圧印加時と無印加時の光の吸収の差が小さくなり、コントラストの向上効果が十分ではない。その為に、用いる液晶に対して0.1～5重量%の範囲で使用することが好ましい。更には1～3重量%の濃度に溶解させるのが好ましい。

【0012】本発明で使用する液晶エマルジョンは従来公知の液晶エマルジョン法によるものでも、又、相分離法によるものであってもよく、特に限定されないが、エマルジョン法によるものが好ましい。液晶エマルジョンは前記液晶を適当なマトリックス樹脂を含む水溶液中に乳化分散させることによって得られる。マトリックス水溶液に上記液晶を分散させる方法としては、超音波分散機等の各種の攪拌装置による混合方法や、膜乳化法（中島忠夫・清水政高、PHARMTECH JAPAN 4巻、10号（1988）参照）等の分散方法が有効である。液晶エマルジョン粒子の大きさは、用いる分散方法に依存するが、一般的には平均粒径が0.5～7μmの範囲にあることが好ましく、1～5μmの範囲であることが更に好ましい。液晶エマルジョンの作製に使用するマトリックス樹脂としては、PVAが好ましく用いら

れるが、ゼラチン、アクリル酸共重合体、水溶性アルキド樹脂等、水に分散若しくは溶解するものであればよい。

【0013】液晶とマトリックス樹脂の使用量としては、マトリックス樹脂／液晶の混合比（重量比）が5/95～50/50であり、液晶の使用量が少なすぎると、電圧オン時の透明性が不足するだけでなく、膜を透明状態にする為に多大の電圧を必要とする等の点で不十分であり、一方、液晶の使用量が多すぎると、電圧オフ時の散乱（濁度）が不足するだけでなく、膜の強度が低下したりするので好ましくない。本発明の液晶／高分子複合型光学素子を形成する為の基板としては、少なくともいずれか一方が、例えば、ITO、SnO<sub>2</sub>系、ZnO系の様な透明導電性を付与したガラスや高分子フィルム等の様な一対の基板である。

【0014】次に本発明の液晶光学素子の製造方法を説明する。図1は本発明の好ましい1実施態様の液晶光学素子の製造工程を図解的に説明する図である。先ず、図1（1）に示す様に、透明基板1の表面にITO膜等の透明導電膜2が形成されており、透明導電膜2上に親水性部分3と撥水性部分4を形成する。ITO、SnO<sub>2</sub>系、ZnO系の様な透明導電性被膜は通常親水性であるので、そのまま親水性部分3として使用してもよい（図示の例）し、又、膜面を粗面化したり、親水性被膜を形成して親水性を更に向上させてもよい。例えば、親水性部分3の好ましい形成方法の1例はアルミニウム等の金属を10～1,000Å程度の非常に薄い膜として蒸着する方法である。この様なアルミニウム膜は充分な親水性を有している。かかるアルミニウム蒸着層は基板全面に形成してもよく、任意のパターン状に形成してもよい。

【0015】一方、撥水性部分4は必ずしも透明である必要はなく、例えば、黒色に着色しておくことによって、素子形成後のブラックマトリックスとして作用させることが出来る。かかる撥水性部分4は、シリコン樹脂、弗素樹脂、乾性油、各種レジスト等の如き撥水性材料からなるインキを調製し、このインキによってシルクスクリーン等で印刷及び乾燥・硬化させることによって、厚み0.1～1μm程度の任意のパターン状に形成することが出来る。この撥水性部分4は、前記親水性部分3が全面に形成されている場合にはその上に任意のパターン状に形成することが出来、又、前記親水性部分3がパターン状に形成されている場合には、該パターンの外縁に同調させて印刷形成することが出来る。これらの撥水性部分4は、着色しても着色しなくてもよいが、色が異なり且つ隣接する親水性部分3上に形成される液晶／高分子複合膜の色と色の混合が生じない様に、光透過性に着色することが好ましい。撥水性部分4の着色は撥水性部分4の作製後に染料や塗料等で行ってよいし、疎水性インキ中に予め染料を溶解させておいたり顔

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料等を分散させておいて、撥水性部分4を作製してもよい。

【0016】次に気泡を十分に取り除いた液晶エマルジョン5を基板全面に塗布すると、図1(2)に示す様に、液晶エマルジョン5は親水性部分3上にのみ残り、撥水性部分4には存在しない。液晶エマルジョン5を塗付する方法としては、流延、刷毛塗り、スプレー、ブレードコーティング、ドクターコーティング等いずれの方法でもよい。液晶エマルジョン5を塗布後、室温又は液晶エマルジョンに影響を与えない程度の温度で乾燥させると、図1(3)に示す様に、親水性部分3のパターンに同調した液晶/高分子複合膜6が得られる。この様な液晶/高分子複合膜6の厚みは通常は3~15 $\mu$ m程度であるのが好ましい。最後の図1(4)に示す様に、透明導電膜1'を形成した対向基板2'の透明導電膜面を上記液晶/高分子複合膜6に向けて貼り合わせることで、気泡や空間を残すことなく密着させて本発明の液晶表示素子が得られる。

【0017】

【実施例】次に実施例を挙げて本発明を更に具体的に説明する。

実施例1

ガラス基板のITO膜上に、アモルファス弗素樹脂(サイトップCTX-805、旭ガラス(株)製)の溶液をスピンコート法で全面に塗布及び加熱乾燥して撥水性部分(膜厚:0.2 $\mu$ m)を形成した。次いで表示部となる液晶/高分子複合膜を形成すべき箇所以外をマスキングし、露出部分にアルミニウムの蒸着を行なって、親水性部分(厚み100Å)を作製した。一方、ネマチック液晶(BL-010、メルク社製)をポリビニルアルコールKP-06(日本合成化学工業(株)製)の10重量%水溶液に膜乳化法で分散させた液晶エマルジョンを作製し、この液晶エマルジョンを撥水性部分と親水性部分とを有する基板全面に塗布し、乾燥させたところ、アルミニウムが蒸着された親水性部分にのみ液晶/高分子複合膜が形成された。次いで、ITO付きポリエチレンテレフタレートフィルム(膜厚125 $\mu$ m、帝人(株)製)を液晶/高分子複合膜を含む全面にラミネートし、周囲を紫外線硬化型シール剤で固定することによって、本発明の液晶光学素子を作製した。この液晶光学素子において、液晶/高分子膜とITO付きポリエチレンテレフタレート膜は完全に密着しており、該素子は電圧を印

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加しなければ白色不透明であるが、電圧を印加すると速やかに無色透明になった。

【0018】実施例2

ITO付きガラス基板の液晶/高分子複合膜を形成すべき箇所以外をマスキングし、アモルファス弗素樹脂サイトップCTX-805(旭ガラス(株)製)をディップコート法で塗工及び加熱乾燥した後、マスキング材を剥離し、撥水性部分(膜厚:0.2 $\mu$ m)と表示部となる親水性部分を形成した。一方、二色性色素(G-264、(株)日本感光色素研究所製)を溶解させたネマチック液晶(BL-010、メルク社製)をポリビニルアルコールKP-06(日本合成化学工業(株)製)の10重量%水溶液に膜乳化法で分散させた液晶エマルジョンを作製し、この液晶エマルジョンを撥水性部分と親水性部分とを有する基板全面に塗布し、乾燥させたところ親水性部分であるITO部分にのみ液晶/高分子複合膜が形成された。次いで、ITO付きポリエチレンテレフタレートフィルム(膜厚125 $\mu$ m、帝人(株)製)を液晶/高分子複合膜を含む全面にラミネートし、周囲を紫外線硬化型シール剤で固定することによって、本発明の液晶光学素子を作製した。この液晶光学素子において、液晶/高分子膜とITO付きポリエチレンテレフタレート膜は完全に密着しており、該素子は電圧を印加しなければ青色不透明であるが、電圧を印加すると速やかに無色透明になった。

【0019】

【効果】以上の如き本発明によれば、パターンコートが極めて容易であり、液晶エマルジョンの浪費がなく且つ液晶光学素子における液晶/高分子複合膜中に気泡が全く含有していない表示特性に優れた液晶光学素子を提供することが出来る。

【0020】

【図面の簡単な説明】

【図1】本発明の好ましい1実施態様の液晶光学素子の製造工程を図解的に説明する図。

【符号の説明】

- 1, 1': 透明基板
- 2, 2': 透明導電膜
- 3: 親水性部分
- 4: 撥水性部分
- 5: 液晶エマルジョン
- 6: 液晶/高分子複合膜

(5)

特開平7-134288

【図1】

